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(54) Method of cold start-up of a PEM fuel cell

Verfahren zum Kaltstarten einer PEM-Brennstoffzelle

Procédé de démarrage à froid de piles à combustible à membrane électrolytique polymère

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- **PATENT ABSTRACTS OF JAPAN vol. 013, no. 018 (E-704), 17 January 1989 (1989-01-17) & JP 63 225477 A (MITSUBISHI ELECTRIC CORP), 20 September 1988 (1988-09-20)**
- **PATENT ABSTRACTS OF JAPAN vol. 010, no. 363 (E-461), 5 December 1986 (1986-12-05) & JP 61 158672 A (FUJI ELECTRIC CO LTD), 18 July 1986 (1986-07-18)**
- **PATENT ABSTRACTS OF JAPAN vol. 013, no. 038 (E-709), 27 January 1989 (1989-01-27) & JP 63 236262 A (HITACHI LTD), 3 October 1988 (1988-10-03)**
- **PATENT ABSTRACTS OF JAPAN vol. 016, no. 347 (E-1240), 27 July 1992 (1992-07-27) & JP 04 106877 A (MITSUBISHI ELECTRIC CORP), 8 April 1992 (1992-04-08)**

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Description

TECHNICAL FIELD

[0001] This invention relates to PEM/SPE fuel cells, and more particularly, to a method of starting-up such fuel cells from subfreezing temperatures.

BACKGROUND OF THE INVENTION

[0002] Fuel cells have been proposed as a power source for many applications. So-called PEM (proton exchange membrane) fuel cells [a.k.a. SPE (solid polymer electrolyte) fuel cells] are particularly desirable for both mobile (e.g. electric vehicles) and stationary applications. PEM/SPE fuel cells include a "membrane electrode assembly" (hereafter, MEA) comprising a thin proton-conductive (i.e. H^+ -conductive), solid-polymer, membrane-electrolyte, having an anode on one of its faces and a cathode on the opposite face. The solid-polymer membranes are typically made from ion exchange resins such as perfluorinated sulfonic acid. One such resin is NAFION[™] sold by the DuPont Company. Such membranes are well known in the art and are described in U.S. Patent 5,272,017 and 3,134,697 as well as in the Journal of Power sources, Vol. 29, (1990), pages 367-387, *inter alia*. The anode and cathode typically comprise finely divided catalytic particles either alone or supported on the internal and external surfaces of carbon particles, and have proton conductive resin intermingled therewith. The anode and cathode catalysts cover opposite faces of a solid polymer membrane electrolyte.

[0003] The MEA is sandwiched between a pair of electrically conductive current collectors for the anode and cathode. The current collectors contain channels/grooves on the faces thereof defining a "flow field" for distributing the fuel cell's gaseous reactants (i.e. H_2 and O_2) over the surfaces of the respective anode and cathode catalysts. Hydrogen is the anode reactant (i.e. fuel) and can either be in a pure form or derived from the reformation of methanol, gasoline or the like. Oxygen is the cathode reactant (i.e. oxidant), and can be either in a pure form or diluted with nitrogen (e.g. air). The overall electrochemical reaction occurring at the MEA under normal fuel cell operation is: (1) H_2 is oxidized on the anode catalyst to form $2H^+$ ions and releases 2 electrons to the external circuit; (2) the H^+ ions move through the membrane to its cathode side; (3) the 2 electrons flow through the external circuit to the cathode side of the membrane where they reduce the O_2 on the cathode catalyst to form O^{2-} ions; and (4) The O^{2-} ions react with the H^+ ions on the cathode side of the membrane to form water.

[0004] Document DE-A-40 33 286 describes a method of operating a solid oxide fuel cell in which H_2 is added to O_2 at the negative electrode in order to cause an exothermal chemical reaction of the H_2 with the O_2 for

heating the fuel cell during a start-up period of the fuel cell and/or for controlling the performance and temperature of the fuel cell during its operation. The solid oxide fuel cell includes an electrolyte made from a solid ceramic material on the basis of zircon oxide which is electrically conductive at high temperatures. The cell is therefore operated at a temperature range between 700 °C and 1200 °C. In order to optimize the energy conversion efficiency of the solid oxide fuel cell, the H_2 and O_2 containing process gases are heated to the reaction temperature of about 800 °C to 1000 °C prior to being introduced to the cell.

[0005] Document JP-A-63 225477 discloses a method for heating a fuel cell in which a mixed gas of hydrogen and oxygen is supplied to at least one of an oxidizer electrode and a fuel electrode, and hydrogen is made to react to oxygen in a catalyst layer of the electrode so that heat is generated to heat the fuel cell.

[0006] It is desirable for many applications, and particularly electric vehicle applications (i.e. to meet customer expectations), that the fuel cell be capable of being started-up quickly so as to be immediately available to produce the energy needed to propel the vehicle without significant delay. At high ambient temperatures (e.g. about 20 °C or more), the fuel cell stack (i.e. plurality of individual cells bundled together into a high voltage pack) can be started-up in a reasonable amount of time because electrical current can be immediately drawn from the stack which, in turn, causes electrical IR-heating of the stack to quickly heat up the stack to its preferred operating temperature (i.e. about 80 °C). At subfreezing temperatures below about -25 °C, however, rapid start-up is much more difficult, because at these temperatures the rate at which the overall electrochemical reaction occurring at the membrane-electrode-assembly takes place is significantly reduced thereby limiting the amount of current that can be drawn from the stack, and hence the IR-heating that can be inputted to the stack. The precise mechanism for the reaction rate reduction is not known. However, it is believed to be that either (1) the H^+ ion conductivity of the solid polymer membrane electrolytes is so poor at these temperatures, (2) or the effectiveness of the catalysts to electrochemically ionize the H_2 and/or O_2 is so poor at these temperatures, that no significant amount of electrical current can be drawn from the stack, and no corresponding IR-heating thereof can occur.

[0007] It is the underlying object of the invention to improve the cold start-up properties of PEM fuel cells at subfreezing temperatures.

SUMMARY OF THE INVENTION

[0008] The object of the invention is satisfied by the methods of heating the membrane electrode assembly of a PEM fuel cell according to either one of claims 1, 11 and 14.

[0009] The present invention comprehends a method

of heating the MEA of a PEM fuel cell while it is cold to thaw it out and thereby accelerate cold start-up of the fuel cell. The method applies to single cells as well as a stack of such cells. The fuel cell has a MEA that comprises a proton-conductive membrane, a cathode catalyst supported on a first face of the membrane, and an anode catalyst supported on a second face of the membrane opposite the first face. In accordance with the present invention, the MEA is thawed out by locally heating it using the heat generated by the exothermal chemical reaction between H_2 and O_2 on the anode and/or cathode catalyst(s) which raises the MEA's temperature from a first subfreezing temperature to a second temperature which is above the first temperature and which enhances the rate of the overall electrochemical reaction occurring at the MEA. More specifically, the method of the present invention comprises the steps of: (1) supplying a H_2 -rich gas (e.g. pure H_2 or CO-containing reformat) to the anode catalyst at a temperature that is above said first temperature and a O_2 -rich gas (e.g. pure O_2 or air) to the cathode catalyst; (2) introducing a sufficient quantity of H_2 into the O_2 -rich gas, and/or a sufficient quantity of O_2 into the H_2 -rich gas to exothermally chemically react the H_2 with the O_2 , and thereby assist in heating the MEA up to a second temperature where current can be drawn from the fuel cell; (3) discontinuing the introduction of such quantities of H_2 and/or O_2 after the MEA reaches a suitable temperature at or above the second temperature; and (4) drawing electrical current from the fuel cell to assist in completing the heating of the fuel cell up to its normal operating temperature.

[0010] The H_2 -rich gas that fuels the anode may be the source of the H_2 provided to the O_2 -rich cathode gas, and air may be the source of the O_2 provided to the H_2 -rich gas. The amount of H_2 introduced into the O_2 -rich gas is such as would produce a mix having a hydrogen content of about 0.5% to about 3.5 % by volume. O_2 concentrations as low as about 1% and as high as 7% by volume (i.e. when mixed with the H_2 -rich gas) can be used when pure H_2 is the fuel. When CO-containing H_2 -rich gases (e.g. reformat) are used, O_2 concentrations between 2% and about 7% by volume are preferred.

[0011] The faces of the membrane that support the catalysts each has (1) a leading edge that first contacts the O_2 -rich/ H_2 -rich gas (es), and (2) a trailing edge that last contacts O_2 -rich/ H_2 -rich gases as the gas (es) flow over the appropriate cathode or anode face. During the thawing step of this invention, the O_2 -rich and/or H_2 -rich gases may be flowed across their associated MEA faces from the leading edge toward the trailing edge at a flow rate greater than the flow rate used for the normal operation of the fuel cell once it has reached its normal operating temperature. This higher rate insures that much of the O_2 and/or H_2 , as appropriate, is/are swept downstream of the leading edge to react on catalyst downstream of the leading edge so as to heat the MEA more evenly than would occur if the O_2/H_2 gas were

flowed at a slower rate and mostly reacted near the leading edge. In this regard, slow flow rates tends to increase the residence time of the O_2/H_2 near the leading edge which causes more of the O_2/H_2 to react thereat causing uneven heating of the MEA. Hence by way of example, if the flow rate of H_2 through a given stack during normal operations were 0.01 kg/min., a useful flow rate during MEA thawing might be about 0.04 kg/min. Similarly, if the flow rate of O_2 through a given stack during normal operations were 0.16 kg/min., a useful flow rate during MEA thawing might be about 0.64 kg/min. Alternatively, the gas flow channels through which the O_2 -rich and H_2 -rich gases flow could be configured (e.g. tapered) such that the gas velocity therein changes from a first higher velocity at the leading edge to a second lower velocity downstream of the leading edge which will also serve to effect more even heating of the MEA.

[0012] If the fuel cell stack were shut down "wet" (i.e. with free water present), ice could form atop the catalyst(s) when the stack is subjected to freezing temperatures. Such ice could block access to the catalyst(s) by the H_2 and/or O_2 and prevent the desired chemical reaction from occurring. In the event of such icing, the dry H_2 -rich gas and, preferably, also the O_2 -rich gas are warmed (i.e. above the temperature of the MEA) and passed through the associated flow field(s) for a sufficient time to de-ice the catalyst(s) before introducing the O_2 and/or H_2 into the fuel or oxidant streams.

[0013] The present invention will better be understood when considered in the light of the following detailed description of one embodiment thereof which is given hereafter in conjunction with the Figure in which:

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] The Figure is a simplified schematic of a fuel cell system according to the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0015] The Figure depicts a simplified schematic of a fuel cell system in accordance with the present invention. In this embodiment, a fuel processor (e.g. reformer) is used to produce a CO-containing, H_2 -rich fuel gas. Alternatively, the H_2 -rich gas could be sourced from tanked H_2 , adsorbed H_2 (e.g. on carbon), or chemically bound hydrogen (e.g. metal hydride). In the embodiment shown, a hydrogen-containing fuel (e.g. methanol, or gasoline) 2 is supplied to a fuel processor 4 (e.g. steam reformer or autothermal reactor) that catalytically dissociates the fuel into an H_2 -rich reformat 6 comprising H_2 , CO_2 , H_2O and CO. The CO content of the reformat 6 is usually too high for the fuel cell stack 8 to accommodate - so the reformat 6 passes one or more CO clean-up devices 10 which typically includes a water gas shift reactor and a preferential oxidation reactor, both of which are well known in the art and do not form a part of the present invention. After the CO content has

been reduced to satisfactory levels, the reformat feed stream 12 is fed to the fuel cell stack 8. As a final CO-cleanup measure, a small amount of air (i.e. less than 8 % by volume) is fed into the feed stream 12 via a metering device 14 at the entrance to the stack 8. The metering device 14 may comprise any one of a variety of devices such as a variable orifice injector, a pulse width modulated injector or a fixed-displacement type device so long as it is capable of modulating the flow of air. The air for the metering device 14 is provided by a compressor 16, and is heated therein incident to the heat of compression that is produced in the compressor 16. The compressor 16 also produces compressed air 18 for the cathode side of the fuel cell stack 8 which cathode air is humidified in a humidifier 20 positioned downstream of the compressor 16. A pressure regulator 22 insures that the air supplied to the fuel cell 8 is at an appropriate pressure.

[0016] In accordance with the present invention, sufficient O₂ (i.e. as air) is provided to the H₂-rich feed stream for the anode side of the stack 8 and/or sufficient H₂ supplied to the O₂-rich feed stream for the cathode side of the stack 8 when the stack is at a temperature below about -25 °C to heat-up the MEA(s) in the stack to a temperature of at least about -20 °C, at which latter temperature electrical current can be drawn from the stack and internal IR heating of the stack begun. Thermal start-up of the stack 8 can further be effected by heating the coolant (e.g. with a combustor) that normally circulates through the stack 8 to cool it. Once the stack 8 is up to temperature, heating of the stack coolant is discontinued, and it resumes its normal cooling function. Preferably, the O₂ and/or H₂ used for heating/thawing will continue to flow until the stack has reached a temperature of at least about 0°C to supplement the IR-heating below freezing.

[0017] The O₂ (e.g. as air) can conveniently be supplied to the anode side of the stack 8 via the same metering device 14 that is used for supplying air for the final CO clean-up, *supra*, during normal operation of the stack. However, for the exothermic heating purpose of the present invention, the O₂ will be supplied to the anode side at a rate sufficient to yield a feed stream having an O₂ content of at least 2% by volume and less than about 7% by volume. Once the temperature of the MEA is raised sufficiently (i.e. to above about 0°C), the O₂ flow rate is reduced down to the desired CO-cleanup level (i.e. less than 1.6 % by volume). Similarly, the H₂ is supplied to the air stream 24 to the stack 8 via line 26 and metering device 28. The H₂ will be supplied to the cathode side of the stack 8 at a rate sufficient to yield an air stream 24 having an H₂ content of at least about 0.5 % by volume and less than about 3.5% by volume. A H₂ sensor 30 monitors the H₂ concentration in the air stream 24, and can be coupled to appropriate devices for controlling the H₂ flow rate.

[0018] Because of the cold temperatures, little if any reaction occurs between the H₂ and O₂ until the gas

streams are contacted by the catalysts that form the anode and cathode faces of the membrane. When such contact is made, an exothermic reaction occurs and the heat therefrom is transmitted directly into the MEA. If the stack was shutdown "wet", some ice may form over the catalyst(s) when the stack is frozen. Such ice formation can inhibit contact between the catalysts and the H₂ - O₂, but can readily be removed by heating the feed stream 12 and air stream 24 and flowing them over the catalyst to melt the ice and carry away the water formed before admitting the O₂ and H₂ to their appropriate streams.

[0019] While the invention has been described in terms of specific embodiments thereof, it is not intended to be limited thereto but rather only to the extent set forth hereafter in the claims which follow.

Claims

1. A method of heating a membrane electrode assembly of a PEM fuel cell (8) from a first subfreezing temperature to a second temperature above said first temperature that enhances the rate of the overall electrochemical reaction occurring at the membrane-electrode-assembly, said fuel cell (8) having a membrane-electrode-assembly comprising a proton-conductive membrane, a cathode catalyst supported on a first face of said membrane, and an anode catalyst supported on a second face of said membrane opposite said first face, comprising the steps of:
 - a) supplying a H₂-rich gas (12) to said anode catalyst at a temperature above said first temperature and above the temperature of the membrane-electrode-assembly and for a sufficient time to de-ice said anode and/or cathode catalyst;
 - b) supplying an O₂-rich gas (24) to said cathode catalyst; and
 - c) introducing sufficient H₂ into said O₂-rich gas (24) to exothermally chemically react said H₂ with said O₂-rich gas (24) on said cathode catalyst to heat said membrane-electrode-assembly to said second temperature.
2. The method according to claim 1 wherein said O₂-rich gas (24) is supplied at a temperature that is above said first temperature.
3. The method according to claim 1 including the step of introducing sufficient O₂ into said H₂-rich gas (12) to exothermally chemically react said O₂ with sufficient H₂ in said H₂-rich gas (12) on said anode catalyst so as to further heat said membrane-electrode-assembly to said second temperature.

4. The method according to claim 1 wherein the concentration of said H₂ in said O₂-rich gas (24) is 0.5% to 3.5% by volume.
5. The method according to claim 1 wherein said first face has a leading edge that first contacts said O₂-rich gas (24) and a trailing edge that last contacts said O₂-rich gas (24) as said O₂-rich gas (24) flows over said face, said O₂-rich gas (24) is flowed across said first face from said leading edge toward said trailing edge at a first rate during the normal operation of said fuel cell (8), and said O₂-rich gas (24) is flowed across said first face at a second rate greater than said first rate during chemical heating of the membrane-electrode-assembly whereby more of said O₂-rich gas (24) is swept downstream of said leading edge to react on cathode catalyst downstream of said leading edge and thereby heat said membrane more evenly than if the O₂-rich gas (24) were flowed at said first rate.
6. The method according to claim 2 wherein said O₂-rich gas (24) is supplied to said cathode catalyst for a sufficient period of time before the introduction of said H₂ to remove any ice from the surface of said cathode catalyst that might otherwise impede the H₂-O₂ chemical reaction that is to occur on said cathode catalyst.
7. The method according to claim 1 wherein said H₂-rich gas (12) is supplied to said anode catalyst for a sufficient period of time before the introduction of said O₂ to remove any ice from the surface of said anode catalyst that might otherwise impede the H₂-O₂ chemical reaction that is to occur on said anode catalyst.
8. The method according to claim 1 wherein said first face has a leading edge that first contacts said O₂-rich gas (24) and a trailing edge that last contacts said O₂-rich gas (24) as said O₂-rich gas (24) flows over said face, and said O₂-rich gas (24) is flowed over said first face from said leading edge toward said trailing edge at a rate that varies from a first velocity at said leading edge to a second velocity at said trailing edge that is less than said first velocity to heat said membrane substantially evenly.
9. The method according to claim 1 wherein said H₂-rich gas (12) is the source of said H₂.
10. The method according to claim 1 wherein air is the source of said O₂.
11. A method of heating membrane-electrode-assembly of a PEM fuel cell (8) from a first subfreezing temperature to a second temperature above said first temperature that enhances the rate of the overall electrochemical reaction occurring at the membrane-electrode-assembly, said fuel cell (8) having a membrane-electrode-assembly comprising a proton-conductive membrane, a cathode catalyst supported on a first face of said membrane, and an anode catalyst supported on a second face of said membrane opposite said first face, comprising the steps of:
 - a) supplying a CO-free, H₂-rich gas (12) to said anode catalyst at a temperature above said first temperature and above the temperature of the membrane-electrode-assembly and for a sufficient time to de-ice said anode and/or cathode catalyst;
 - b) supplying an O₂-rich gas (24) to said cathode catalyst; and
 - c) introducing sufficient O₂ into said CO-free, H₂-rich gas (12) to exothermally chemically react with sufficient H₂ in said H₂-rich gas (12) on said anode catalyst to heat said membrane-electrode-assembly to said second temperature.
12. The method according to claim 11 wherein said O₂-rich gas (24) is supplied at a temperature that is above said first temperature.
13. The method according to claim 11 wherein the concentration of said O₂ in said H₂-rich gas (12) is about 1% to about 7% by volume.
14. A method of heating a membrane-electrode-assembly of a PEM fuel cell (8) from a first subfreezing temperature to a second temperature above said first temperature that enhances the rate of the overall electrochemical reaction occurring at the membrane-electrode-assembly, said fuel cell (8) having a membrane-electrode-assembly comprising a proton-conductive membrane, a cathode catalyst supported on a first face of said membrane, and an anode catalyst supported on a second face of said membrane opposite said first face, comprising the steps of:
 - a) supplying a CO-containing, H₂-rich gas (12) to said anode catalyst at a temperature above said first temperature and above the temperature of the membrane-electrode-assembly and for a sufficient time to de-ice said anode and/or cathode catalyst;
 - b) supplying an O₂-rich gas (24) to said cathode catalyst; and
 - c) introducing about 2% to about 7% by volume O₂ into said CO-containing, H₂-rich gas (12) to exothermally chemically react with sufficient H₂ in said H₂-rich gas (12) on said anode catalyst to heat said membrane-electrode-assembly to

said second temperature.

15. The method according to claim 14 wherein said O₂-rich gas (24) is supplied at a temperature that is above said first temperature.

Patentansprüche

1. Verfahren zum Erwärmen einer Membranelektrodenanordnung einer PEM-Brennstoffzelle (8) von einer ersten Temperatur unterhalb des Gefrierpunktes zu einer zweiten Temperatur oberhalb der ersten Temperatur, was die Rate der gesamten elektrochemischen Reaktion steigert, die an der Membranelektrodenanordnung stattfindet, wobei die Brennstoffzelle (8) eine Membranelektrodenanordnung mit einer protonenleitenden Membran, einem Kathodenkatalysator, der auf einer ersten Seite der Membran getragen ist, und einem Anodenkatalysator umfasst, der auf einer zweiten Seite der Membran gegenüberliegend der ersten Seite getragen ist, mit den Schritten, dass:

- a) ein H₂-reiches Gas (12) an den Anodenkatalysator mit einer Temperatur oberhalb der ersten Temperatur und oberhalb der Temperatur der Membranelektrodenanordnung für eine ausreichende Zeitdauer geliefert wird, um den Anoden- und/oder Kathodenkatalysator zu ent-eisen;
- b) ein O₂-reiches Gas (24) an den Kathodenkatalysator geliefert wird; und
- c) ausreichend H₂ in das O₂-reiche Gas (24) eingeführt wird, um das H₂ mit dem O₂-reichen Gas (24) exotherm an dem Kathodenkatalysator chemisch zu reagieren und damit die Membranelektrodenanordnung auf die zweite Temperatur zu erwärmen.

2. Verfahren nach Anspruch 1, wobei das O₂-reiche Gas (24) mit einer Temperatur geliefert wird, die über der ersten Temperatur liegt.
3. Verfahren nach Anspruch 1, mit dem Schritt, dass ausreichend O₂ in das H₂-reiche Gas (12) eingeführt wird, um das O₂ mit ausreichend H₂ in dem H₂-reichen Gas (12) exotherm an dem Anodenkatalysator chemisch zu reagieren und somit die Membranelektrodenanordnung weiter auf die zweite Temperatur zu erwärmen.
4. Verfahren nach Anspruch 1, wobei die Konzentration des H₂ in dem O₂-reichen Gas (24) zwischen 0,5 Vol.-% bis zu 3,5 Vol.-% liegt.
5. Verfahren nach Anspruch 1, wobei die erste Seite einen vorausgehenden Rand

aufweist, der zuerst mit dem O₂-reichen Gas (24) in Kontakt tritt, und einen nachfolgenden Rand aufweist, der mit dem O₂-reichen Gas (24) zuletzt in Kontakt tritt, wenn das O₂-reiche Gas (24) über die Seite strömt, das O₂-reiche Gas (24) während des Normalbetriebs der Brennstoffzelle (8) über die erste Seite von dem vorausgehenden Rand in Richtung des nachfolgenden Randes mit einer ersten Rate strömt und das O₂-reiche Gas (24) während einer chemischen Erwärmung der Membranelektrodenanordnung über die erste Seite mit einer zweiten Rate strömt, die größer als die erste Rate ist, wodurch mehr O₂-reiches Gas (24) stromabwärts des vorausgehenden Randes zur Reaktion an dem Kathodenkatalysator unterstromig des vorausgehenden Randes gespült wird, wodurch die Membran gleichmäßiger erwärmt wird, als wenn das O₂-reiche Gas (24) mit der ersten Rate strömen würde.

6. Verfahren nach Anspruch 2, wobei das O₂-reiche Gas (24) an den Kathodenkatalysator für eine ausreichende Zeitdauer vor der Einführung des H₂ geliefert wird, um jegliches Eis von der Oberfläche des Kathodenkatalysators zu entfernen, das ansonsten die chemische Reaktion zwischen H₂ und O₂ behindern würde, die an dem Kathodenkatalysator stattfinden soll.
7. Verfahren nach Anspruch 1, wobei das H₂-reiche Gas (12) an den Anodenkatalysator für eine ausreichende Zeitdauer vor der Einführung des O₂ geliefert wird, um jegliches Eis von der Oberfläche des Anodenkatalysators zu entfernen, das ansonsten die chemische Reaktion zwischen H₂ und O₂ behindern könnte, die an dem Anodenkatalysator stattfinden soll.
8. Verfahren nach Anspruch 1, wobei die erste Seite einen vorausgehenden Rand, der zuerst mit dem O₂-reichen Gas (24) in Kontakt tritt, und einen nachfolgenden Rand aufweist, der zuletzt mit dem O₂-reichen Gas (24) in Kontakt tritt, wenn das O₂-reiche Gas (24) über die Seite strömt, und das O₂-reiche Gas (24) über die erste Seite von dem vorausgehenden Rand in Richtung des nachfolgenden Randes mit einer Rate strömt, die von einer ersten Geschwindigkeit an dem vorausgehenden Rand zu einer zweiten Geschwindigkeit an dem nachfolgenden Rand variiert, welche kleiner als die erste Geschwindigkeit ist, um die Membran im Wesentlichen gleichmäßig zu erwärmen.
9. Verfahren nach Anspruch 1, wobei das H₂-reiche Gas (12) die Quelle des H₂ darstellt.
10. Verfahren nach Anspruch 1, wobei Luft die Quelle des O₂ darstellt.

11. Verfahren zum Erwärmen einer Membranelektrodenanordnung einer PEM-Brennstoffzelle (8) von einer ersten Temperatur unterhalb des Gefrierpunktes zu einer zweiten Temperatur oberhalb der ersten Temperatur, was die Rate der gesamten elektrochemischen Reaktion steigert, die an der Membranelektrodenanordnung stattfindet, wobei die Brennstoffzelle (8) eine Membranelektrodenanordnung mit einer protonenleitenden Membran, einem Kathodenkatalysator, der auf einer ersten Seite der Membran getragen ist, und einem Anodenkatalysator umfasst, der auf einer zweiten Seite der Membran gegenüberliegend der ersten Seite getragen ist, mit den Schritten, dass:

- a) ein CO-freies und H₂-reiches Gas (12) an den Anodenkatalysator mit einer Temperatur oberhalb der ersten Temperatur und oberhalb der Temperatur der Membranelektrodenanordnung für eine ausreichende Zeitdauer geliefert wird, um den Anoden- und / oder Kathodenkatalysator zu enteisen;
- b) ein O₂-reiches Gas (24) an den Kathodenkatalysator geliefert wird, und
- c) ausreichend O₂ in das CO-freie und H₂-reiche Gas (12) eingeführt wird, der mit ausreichend H₂ in dem H₂-reichen Gas (12) exotherm an dem Anodenkatalysator chemisch reagiert, um die Membranelektrodenanordnung auf die zweite Temperatur zu erwärmen.

12. Verfahren nach Anspruch 11, wobei das O₂-reiche Gas (24) bei einer Temperatur geliefert wird, die über der ersten Temperatur liegt.

13. Verfahren nach Anspruch 11, wobei die Konzentration des O₂ in dem H₂-reichen Gas (12) zwischen etwa 1 Vol.-% und etwa 7 Vol.-% liegt.

14. Verfahren zum Erwärmen einer Membranelektrodenanordnung einer PEM-Brennstoffzelle (8) von einer ersten Temperatur unterhalb des Gefrierpunktes zu einer zweiten Temperatur oberhalb der ersten Temperatur, was die Rate der gesamten elektrochemischen Reaktion steigert, die an der Membranelektrodenanordnung stattfindet, wobei die Brennstoffzelle (8) eine Membranelektrodenanordnung mit einer protonenleitenden Membran, einem Kathodenkatalysator, der auf einer ersten Seite der Membran getragen ist, und einem Anodenkatalysator umfasst, der auf einer zweiten Seite der Membran gegenüberliegend der ersten Seite getragen ist, mit den Schritten, dass:

- a) ein CO-haltiges und H₂-reiches Gas (12) an den Anodenkatalysator mit einer Temperatur oberhalb der ersten Temperatur und oberhalb

der Temperatur der Membranelektrodenanordnung für eine ausreichende Zeitdauer geliefert wird, um den Anoden- und / oder Kathodenkatalysator zu enteisen;

- b) ein O₂-reiches Gas (24) an den Kathodenkatalysator geliefert wird, und
- c) etwa 2 Vol.-% bis etwa 7 Vol.-% O₂ in das CO-haltige und H₂-reiche Gas 12 eingeführt wird, der mit ausreichend H₂ in dem H₂-reichen Gas (12) exotherm an dem Anodenkatalysator chemisch reagiert, um die Membranelektrodenanordnung auf die zweite Temperatur zu erwärmen.

15. Verfahren nach Anspruch 14, wobei das O₂-reiche Gas (24) bei einer Temperatur geliefert wird, die über der ersten Temperatur liegt.

20 Revendications

1. Procédé de chauffage d'un ensemble membrane-électrodes d'une pile à combustible à membrane échangeuse de protons (PEM) (8) à partir d'une première température de sous-congélation jusqu'à une deuxième température supérieure à ladite première température, qui accroît la vitesse de la réaction électrochimique globale ayant lieu dans l'ensemble membrane-électrodes, ladite pile à combustible (8) comportant un ensemble membrane-électrodes comprenant une membrane conduisant les protons, à un catalyseur cathodique supporté par une première face de ladite membrane, et un catalyseur anodique supporté par une deuxième face de ladite membrane opposée à ladite première face, comprenant les étapes consistant à :

- a) fournir un gaz riche en H₂ (12) audit catalyseur anodique, à une température supérieure à ladite première température et supérieure à la température de l'ensemble membrane-électrodes et pendant un temps suffisant pour dégivrer lesdits catalyseurs anodique et/ou cathodique ;
- b) fournir un gaz riche en O₂ (24) audit catalyseur cathodique ; et
- c) introduire suffisamment de H₂ dans ledit gaz riche en O₂ (24) pour faire réagir chimiquement de manière exothermique ledit H₂ avec ledit gaz riche en O₂ (24) sur ledit catalyseur cathodique afin de chauffer ledit ensemble membrane-électrodes jusqu'à ladite deuxième température.

2. Procédé selon la revendication 1, dans lequel ledit gaz riche en O₂ (24) est fourni à une température supérieure à ladite première température.

3. Procédé selon la revendication 1, comprenant l'étape consistant à introduire suffisamment de O_2 dans ledit gaz riche en H_2 (12) afin de faire réagir chimiquement de manière exothermique ledit oxygène avec suffisamment de H_2 dans ledit gaz riche en H_2 (12) sur ledit catalyseur anodique de façon à chauffer davantage ledit ensemble membrane-électrodes jusqu'à ladite deuxième température.
4. Procédé selon la revendication 1, dans lequel la concentration dudit H_2 dans ledit gaz riche en O_2 (24), est de 0,5 % à 3,5 % en volume.
5. Procédé selon la revendication 1, dans lequel ladite première face comporte un bord amont qui rentre le premier en contact avec ledit gaz riche en O_2 (24), et un bord aval qui rentre en dernier en contact avec ledit gaz riche en O_2 (24) lorsque ledit gaz riche en O_2 (24) s'écoule sur ladite surface, ledit gaz riche en O_2 (24) s'écoulant à travers ladite première face à une deuxième vitesse supérieure à ladite première vitesse en cours de chauffage chimique de l'ensemble membrane-électrodes grâce à quoi plus dudit gaz riche en O_2 (24) est balayé en aval dudit bord amont pour réagir sur le catalyseur cathodique en aval dudit bord amont, et chauffer ainsi ladite membrane plus uniformément que si le gaz riche en O_2 (24) s'écoulait à ladite première vitesse.
6. Procédé selon la revendication 2, dans lequel ledit gaz riche en O_2 (24) est fourni audit catalyseur cathodique pendant une période suffisante avant d'introduire ledit H_2 afin d'éliminer toute glace à la surface dudit catalyseur cathodique qui pourrait autrement empêcher la réaction chimique H_2-O_2 qui doit se produire sur ledit catalyseur cathodique.
7. Procédé selon la revendication 1, dans lequel ledit gaz riche en H_2 (12) est fourni audit catalyseur anodique pendant une période suffisante avant d'introduire ledit O_2 afin d'éliminer toute glace de la surface dudit catalyseur anodique qui pourrait autrement gêner la réaction chimique H_2-O_2 qui doit avoir lieu sur ledit catalyseur anodique.
8. Procédé selon la revendication 1, dans lequel ladite première face comporte un bord amont qui rentre en premier en contact avec ledit gaz riche en O_2 (24), et un bord aval qui vient en dernier en contact avec ledit gaz riche en O_2 (24) lorsque ledit gaz riche en O_2 (24) s'écoule sur ladite face, et ledit gaz riche en O_2 (24) s'écoule sur ladite première face dudit bord amont vers ledit bord aval à une vitesse qui varie à partir d'une première vitesse audit bord amont jusqu'à une deuxième vitesse audit bord aval inférieure à ladite première vitesse, afin de chauffer à peu près uniformément ladite membrane.
9. Procédé selon la revendication 1, dans lequel ledit gaz riche en H_2 (12) est la source dudit H_2 .
10. Procédé selon la revendication 1, dans lequel l'air est la source dudit O_2 .
11. Procédé de chauffage d'un ensemble membrane-électrodes d'une pile à combustible à membrane échangeuse de protons (PEM) (8) à partir d'une première température de sous-congélation jusqu'à une deuxième température supérieure à ladite première température, qui accroît la vitesse de la réaction électrochimique globale qui se produit à l'ensemble membrane-électrodes, ladite pile à combustible (8) comportant un ensemble membrane-électrodes comprenant une membrane conduisant les protons, un catalyseur cathodique supporté sur une première face de ladite membrane, et un catalyseur anodique supporté sur une deuxième face de ladite membrane opposée à ladite première face, comprenant les étapes consistant à:
 - a) fournir un gaz riche en H_2 exempt de CO (12) audit catalyseur anodique, à une température supérieure à ladite première température et supérieure à la température de l'ensemble membrane-électrodes et pendant un temps suffisant pour dégivrer lesdits catalyseurs anodique et/ou cathodique ;
 - b) fournir un gaz riche en O_2 (24) audit catalyseur cathodique ; et
 - c) introduire suffisamment de O_2 dans ledit gaz riche en H_2 exempt de CO (12) pour réagir chimiquement de manière exothermique avec suffisamment de H_2 dans ledit gaz riche en H_2 (12) sur ledit catalyseur anodique afin de chauffer ledit ensemble membrane-électrodes jusqu'à ladite deuxième température.
12. Procédé selon la revendication 11, dans lequel ledit gaz riche en O_2 (24) est fourni à une température supérieure à ladite première température.
13. Procédé selon la revendication 11, dans lequel la concentration en ledit O_2 dans ledit gaz riche en H_2 (12), est d'environ 1 % à environ 7 % en volume.
14. Procédé de chauffage d'un ensemble membrane-électrodes d'une pile à combustible à membrane échangeuse de protons (PEM) (8) à partir d'une première température de sous-congélation jusqu'à une deuxième température supérieure à ladite première température, qui accroît la vitesse de la réaction électrochimique globale ayant lieu à l'ensemble membrane-électrodes, ladite pile à combustible (8) comportant un ensemble membrane-électrodes comprenant une membrane conduisant les protons, un catalyseur cathodique supporté par une première

re face de ladite membrane, et un catalyseur anodique supporté par une deuxième face de ladite membrane opposée à ladite première face, comprenant les étapes consistant à:

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a) fournir un gaz riche en H_2 contenant CO (12) audit catalyseur anodique à une température supérieure à ladite première température et supérieure à la température de l'ensemble membrane-électrodes et pendant un temps suffisant pour dégivrer lesdits catalyseurs anodique et/ou cathodique ;

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b) fournir un gaz riche en O_2 (24) audit catalyseur cathodique ; et

c) introduire d'environ 2 % à environ 7 % en volume de O_2 dans ledit gaz riche en H_2 contenant CO (12) afin de réagir chimiquement de manière exothermique avec suffisamment de H_2 dans ledit gaz riche en H_2 (12) sur ledit catalyseur anodique, pour chauffer ledit ensemble membrane-électrodes jusqu'à ladite deuxième température.

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15. Procédé selon la revendication 14, dans lequel ledit gaz riche en O_2 (24) est fourni à une température supérieure à ladite première température.

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